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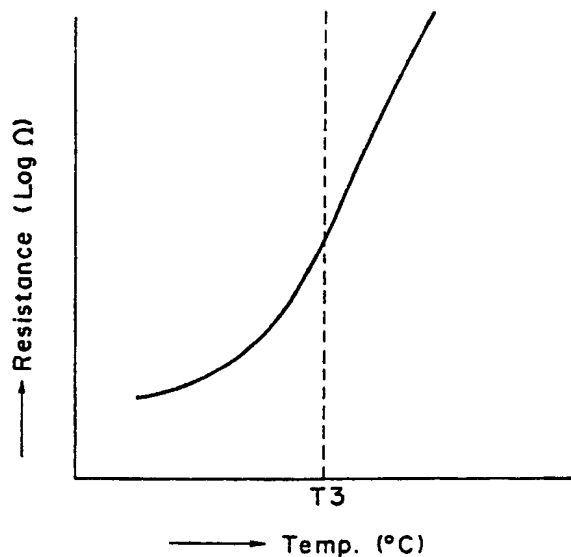
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(54) Temperature self-controlling heating composition.

(57) The present invention provides a temperature self-controlling heating composition containing crystalline resins, elastomers and electrically conductive particles, and additional material for giving an affinity to the resins and the elastomers if the both are not compatible, in which the electrically conductive particles are stably dispersed in the medium of the resin and the elastomer, and the agglomeration of the dispersed particles can be prevented, even if the temperature exceeds the melting point of the crystalline resins, because the apparent viscosity of the resin is not dropped so much by the net work structure of the elastomers, so that the electrical resistance does not drop down even in such a high temperature.

Fig. 2



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Temperature Self-controlling Heating Composition

The present invention relates to a temperature self-controlling heating composition having a positive temperature coefficient (referred to as PTC hereinafter), which can be used for a domestic heater such as a floor heater, a wall heater and the like.

So far a temperature self-controlling heating composition which has been practiced is produced by the radiation crosslinking of a molded article of mixture of crystalline resins such as low density polyethylene and carbon black.

A heating composition produced from a simple mixture of a crystalline resin and carbon black has a tendency that an electrical resistance sharply increases near the softening temperature (T₁) of the crystalline resin and decreases at a temperature higher than the melting point (T₂) as shown by a solid line in Fig. 1. Accordingly, if the heating composition is heated by an outside heat source and the temperature of the composition rises higher than the melting point T₂, the resistance of the composition becomes reduced and the temperature abnormally rises to possible ignition. Further, there is a serious problem that the resistance becomes gradually increased to finally lose the heating ability, if an electrical potential is continuously or intermittently applied to the heating composition even at an ordinary temperature.

As a cause of the above phenomenon a following ground is thought. Though it is formed an electrical conductive path in which carbon black is homogeneously dispersed into a crystalline resin just after both are mixed, the carbon black, at a temperature higher than the melting point (T₂) of the crystalline resin, begins Brownian movement in the melted crystalline resin, and the Brownian movement increases as the temperature becomes higher, so that the opportunity of contact of adjacent carbon black increases. As the result of the above the resistance reduces at a temperature higher than the melting point (T₂) of the crystalline resin. On the other hand, the reason of the increase of the resistance in the latter case is considered that the electrical conductive path is interrupted by partial agglomeration (deterioration of dispersion) of the carbon black which will be induced by continuous or intermittent application of an electrical pressure.

Such agglomeration of carbon black will be caused by lower heat resistance of a crystalline resin, a dispersion medium for the carbon black. A heat saturated temperature of a temperature self-controlling heater is set up at a temperature lower than the melting point of the crystalline resin by about 20 - 30 °C, the reason of which is that the

PCT property is depended on the change of specific volume of the crystalline resin in melted state, and such a selection of the temperature will be suitable. The heat saturated temperature, however, is a macrotemperature of a whole temperature self-controlling heating composition, and the microtemperature in the crystalline resin forming the electrical conductive path will rise higher than or near the melting point in some occasion. The crystalline resin will be sharply reduced in the viscosity at a temperature higher than the melting point to become liquid. The carbon black cannot be retained in the melted resin so as to partially agglomerate, and portions consisting of only the crystalline resin inherently insulative are formed within the electrical conductive path to make the heating composition highly resistive. As apparent from the above reasons, it had been considered difficult to stably retain carbon black dispersed in a crystalline resin alone. Therefore, a conventionally practiced heating composition is produced by the radiation crosslinking of a molded article made from a mixture of carbon black and a crystalline resin. As the crystalline resin subjected to the radiation crosslinking is improved in the heat resistance by the formation of a three-dimensional structure from the crystalline resin having a two-dimensional structure (prevention of the rapid change in physical properties near the melting point, especially decrease of viscosity), the agglomeration of the carbon black can be prevented. The relation of resistance (ordinate) and temperature (abscissa) of such an embodiment is shown in Fig. 1, in which the broken line indicates the resistance/temperature curve.

The temperature self-controlling heating composition containing such a crosslinked resin is too expensive because the cost of equipment for the radiation crosslinking is expensive, and is lack in flexibility.

SUMMARY OF THE INVENTION

The object of the present invention is to provide economically a flexible temperature self-controlling heating composition improved in the aforementioned defects.

The heating composition of the present invention can be provided from a mixture of crystalline resins, elastomers having high temperature resistance and compatibility with said crystalline resin, and electrically conductive particles.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph showing the relation of electrical resistance and temperature in a conventional temperature self-controlling heating composition,

Fig. 2 is a graph showing the relation of electrical resistance and temperature in one embodiment of a temperature self-controlling heating composition of the present invention, and

Fig. 3 is a graph showing the relation of electrical resistance and temperature in another embodiment of a temperature self-controlling heating composition of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The first embodiment of the present invention is a temperature self-controlling heating composition which comprises crystalline resins, elastomers having high temperature resistance and compatibility with the crystalline resins, and electrical conductive particles.

The feature of the present invention is in that the heating composition comprises elastomers having high temperature resistance and compatibility with the crystalline resin. As aforementioned carbon black dispersed in crystalline resins is liable to agglomerate when the temperature of the heating composition rises higher than the melting point, because the resin becomes fluid, and the electrical resistance sharply drops down to lead to a rapid temperature rise in a conventional heating composition. In the present invention the elastomer contained in the composition prevent the electrical conductive particles dispersed in the crystalline resin from agglomerating even when the temperature exceeds the melting point of the crystalline resin, because the melted crystalline resin is retained, due to the compatibility of the elastomer and the resin, in the matrix formed with the net work of the elastomer which has a three dimension structure, and is prevented from remarkable drop of the viscosity. When elastomers incompatible with the crystalline resin are used, a third material, especially resinous material, which is compatible with both of the resin and the elastomer may be additionally mixed with the both in such an amount that the crystalline resin and the elastomer can become mutually miscible. It would be clearly understandable that the same effect as obtained in the first embodiment can be obtained in such an embodiment.

Thus, the second embodiment of the present invention is a temperature self-controlling heating composition which comprises crystalline resins, elastomers having high temperature resistance and incompatible with said resins, materials compatible with both of the resins and the elastomers, and

electrically conductive particles.

The crystalline resin usable in the present invention may include polyethylene, polypropylene, polyoxymethylene, polyvinyl alcohol, modified polyethylene (e.g. maleic anhydride modified polyethylene), polymethylmethacrylate, polyvinylacetate, polyvinylchloride and the like. Polyethylenes including high density polyethylene, low density polyethylene, modified polyethylene and the like are especially interest because of its chemical stability, inert property against any electrical conductive particles, and low price. If crystalline resins having polarity and electrically conductive particles having polarity on the surface such as carbon black are used in the same composition, the particle can be more stably dispersed in the resin due to the affinity induced by the polarities, which is also preferable embodiment.

As examples of the preferable groups causing the polarity on the crystalline resin are hydroxyl groups, carboxyl groups, amino groups, aldehyde groups ether groups, and the like.

The content of the crystalline resin in the composition is preferably about 15 to 60 % by weight, more preferably about 25 to 45 % by weight based on the total amount of the composition.

The elastomers compatible with the crystalline resin (referred to as an elastomer (I)) are preferably selected from elastomers having a solubility parameter different from that of crystalline resin by not more than about 2, more preferably not more than 1.8. The solubility parameter (SP) is defined by the following equation:

$$SP = \sqrt{\frac{\Delta E}{V}}$$

wherein ΔE represents evaporation energy, and V represents molecular volume.

Preferable elastomer (I) is a thermoplastic elastomer. Examples of the elastomer (I) usable in the present invention include, though it depends on the kinds of the crystalline resin, styrene/butadiene rubber, maleic anhydride modified styrene/butadiene rubber, crosslinked ethylene propylene rubber, chlorinated rubber, chlorinated polyolefin and the like in general.

The content of the elastomer (I) in the composition is preferably about 15 to about 60 % by weight, more preferably about 25 to about 45 % by weight based on the total amount of the composition.

The elastomers incompatible with the crystalline resin (referred to as an elastomer (II)) preferably have solubility parameter of more than 2. The elastomer (II) should have a net work structure, and

preferably thermoplasticity, but a melting point fairly higher than that of the crystalline resin to be used together. Preferable examples of the elastomer (II) include polyester type elastomers, polyurethane rubber.

The elastomer (II) should be used together with materials compatible with both of the crystalline resins and the elastomer (II). These materials (referred to as a compatible material hereinafter) act as a mediator between the resin and the elastomer (II) in the composition to form a homogeneous mixture. The compatible materials may be resinous materials, elastomers, plasticizers, waxy materials, and the like, but the most preferable ones are resinous materials, for example, maleic acid modified resin and the like or elastomers. The compatible materials have a solubility parameter between those of the crystalline resin and the elastomer, and the differences in the solubility parameter from the both are not more than about 2, more preferably not more than about 1.8 respectively.

The content of the elastomer (II) is preferably about 15 to about 60 % by weight, more preferably about 25 to about 45 % by weight based on the total amount of the composition. The ratio of the elastomer (II) to the compatible material is not restrictive, but the comparative material is preferably used at the percentage of from about 5 to about 30 based on the total weight of the composition, and the compatible materials should be used at such an amount that the crystalline resin and the elastomer (II) can be homogeneously mixed under the presence of the compatible materials.

The elastomer (II) may be used with an elastomer (I), or together with an elastomer (I) and a compatible material. In the former the elastomer (I) itself acts as a compatible material. In the latter the elastomer (I) may act as a compatible material or not. These embodiments should be, of course, interpreted as one of the embodiment of the present invention.

Electrically conductive particles according to the present invention may be carbon powders such as carbon black, graphite powders and the like; metal powders such as iron powders, copper powders, aluminum powders, nickel powders and the like; powders of ionizable materials such as metal oxides, carbonates, and the like; metal coated powders and the like. Most preferable electrically conductive particles are carbon black, because it is excellent in a dispersability due to its low gravity and affinity to crystalline resins in general, and it has a comparatively high electrical conductivity.

Preferable particle size of the electrically conductive particles is from about 20 to about 100 nm. The dispersability of the particle is improved as the particle size is smaller, but the Brownian movement

becomes more active, and the electrical resistance of the composition is liable to change with the change of the temperature.

In the first embodiment the electrically conductive particles may be directly dispersed into melted crystalline resins, or previously dispersed into a small amount of crystalline resins and then mixed with the same or different melted crystalline resins.

In the second embodiment the electrically conductive particles may be directly dispersed into any of the melted mixture of crystalline resins, elastomers (II) and compatible materials, or previously dispersed into the melted crystalline resins, elastomers (II) and/or the compatible materials to give a master batch, and then the master batch is dispersed into the other rest components, or any other processes may be applicable. If extremely fine particles are used, it is preferable to previously disperse the particles into elastomers (II) to give comparatively large particles, and mix the obtained large particles into melted crystalline resins together with compatible materials. As, in this embodiment, the electrically conductive particles are dispersed in the elastomer (II) having a higher melting point, and the elastomer (II) containing the fine particles are dispersed in the crystalline resins, the fine particles can be restrained in the Brownian movement even when the temperature of the composition exceeds the melting point of the crystalline resins, and the elastomer particles are also restrained because of its largeness. Therefore, the drop of the resistance at that temperature can be prevented.

The content of the electrically conductive particles are extremely depended on the kinds of the particles, especially specific conductivity, particle size, specific gravity and the like. Therefore, it cannot be defined simply, but in case of carbon black, the content is preferably about 10 to about 60 % by weight based on the total amount of the composition, more preferably about 15 % to about 50 %.

The temperature self-controlling heating composition of the present invention may contain another material, for example, electrically conductive resinous material, and so on.

The composition of the present invention can be molded to a plate, a sheet, a film, a rod and the like, or impregnated into or coated on a matrix such as a web, a net, a textile, a paper, a string, a sponge and the like, or coated on a sheet, a plate and the like, or filled into a tube, panels and the like.

The temperature self-controlling heating composition of the present invention is especially useful for a floor heater, a wall heater, a heater for freezing prevention and the like.

The present invention shall be illustrated ac-

cording to following examples, but it should not be construed restrictively by these examples.

Example 1

As a crystalline resin low density polyethylene (mp. 110 °C; Sumikathene E-104 available from Sumitomo Kagaku K.K.) 100 parts by weight, and as an elastomer compatible with the crystalline resin a polystyrene type thermoplastic elastomer (Kraton G 1650, available from Shell Chemical Co., Ltd.) 100 parts by weight were premixed by passing through pressure rolls heated at 170 °C 5 times, and then carbon black (particle size of 80 nm, 67 parts by weight was blended by passing through the same pressure rolls heated at 170 °C 20 times to give a temperature self-controlling heating composition.

The heating composition obtained was rolled at 170 °C to a sheet having a thickness of about 0.7 mm, into which one pair of electrodes of copper wires (ϕ 0.3 mm X 20 mm L) was parallelly buried along the longer side at interval of 1 mm. The obtained material was pressed at 170 °C for 2 hours, and then cooled to give a panel heater (10 mm (L) x 4 mm (W) x 1 mm (T)) for test.

The heater obtained has an electrical resistance of 30 Ω cm at 20 °C, and 200 Ω cm at 80 °C, and effectively and continuously generates heat for more than 10000 hours when applied to with AC 100 V at 100 °C.

Example 2

As a crystalline resin to which a polarity is introduced a maleic anhydride modified high density polyethylene (mp. 130 °C, SP value 8.0, Adomer HB 310, available from Mitsui Sekiyu Kagaku K.K.) 100 parts by weight, as an elastomer compatible with the above resin a maleic anhydride modified polystyrene type thermoplastic elastomer (SP value 9.0, Tuftec M1913 available from Asahi Kasei K.K.) 100 parts by weight were premixed with pressure rolls heated at 170 °C five times. Into the mixture carbon black (particle size of 80 nm, pH 8.0, Diablack G available from Mitsubishi Kasei K.K.) was blended by the same rolls at 170 °C 20 times to give a temperature self-controlling heating composition.

Using the heating composition obtained above a panel heater (10 mm x 4 mm x 1 mm) for test was produced in the same manner as described in the Example 1.

The heater obtained has an electrical resistance of 40 Ω cm at 20 °C, and 180 Ω cm at 80 °C, and effectively and continuously generates

heat for more than 10000 hours when applied to with AC 100 V at 100 °C.

Example 3

Tuflec M1913, elastomer, 29 parts by weight and carbon black (Diablack G) 43 parts by weight were blended by pressure rolls heated at 200 °C 20 times to give a master batch. The obtained master batch 72 parts by weight and Adomer HB-310, crystalline resin, 28 parts by weight were blended by the same rolls at 170 °C 20 times to give a temperature self-controlling heating composition.

A panel heater (10 mm x 4 mm x 1 mm) for test was produced from the obtained heating composition in the same manner as described in the Example 1.

The heater obtained has an electrical resistance/temperature curve shown in Fig. 2, and effectively and continuously generates heat for more than 10000 hours when applied to with AC 100 V at 100 °C.

Example 4

As a crystalline resin a low density polyethylene (mp. 110 °C, SP value 8.1, Sumikathene E 104 available from Sumitomo Kagaku K.K.);

as an elastomer having a heat resistance higher than the above crystalline resin and incompatibility with the same a polyester type thermoplastic elastomer (mp. 182 °C, SP value 10.5, Hytrel 4047 available from Torey Du Pont K.K.);

as a third material compatible with both the crystalline resin and the elastomer a modified low density polyethylene (mp. 107 °C, SP value 9.0, Bondine LX 4110 available from Sumitomo Kagaku K.K.); and

as an electrically conductive particle carbon black (particle size of 80 nm, pH 8.0, Diablack G available from Mitsubishi Kasei K.K.) were used.

The carbon black 23 parts by weight and the elastomer 31 parts by weight were blended by pressure rolls at 200 °C 20 times to give a master batch, with which the crystalline resin 32 parts by weight and the third material 14 parts by weight were blended by the same rolls at 170 °C 20 times to prepare a temperature self-controlling heating composition.

A panel heater (10 mm x 4 mm x 1 mm) for test was produced from the obtained heating composition in the same manner as described in the Example 1.

The heater obtained has an electrical resistance/temperature curve shown in Fig. 3, and

effectively and continuously generates heat for more than 10000 hours when applied to with AC 100 V at 100 °C.

As apparent from Fig. 2 and Fig. 3 heaters obtained from the heating composition of the present invention show excellent PTC property even over the melting point of the crystalline resin (T3) without any drop of resistance. Furthermore, the heater obtained has a flexibility due to the elastomer.

Claims

1. A temperature self-controlling heating composition which comprises:

- (1) crystalline resins,
- (2) elastomers having compatibility with the crystalline resins and heat resistance higher than that of the crystalline resins, and
- (3) electrically conductive particles.

2. A temperature self-controlling heating composition of the Claim 1, in which each content of the crystalline resins, elastomers and the electrically conductive particles is about 15 to about 60 % by weight, about 15 to about 60 % by weight and about 15 to about 60 % by weight in the above order.

3. A temperature self-controlling heating composition of Claim 1 or 2, in which the elastomer possess an affinity to the electrically conductive particles rather than to the crystalline resin.

4. A temperature self-controlling heating composition which comprises:

- (1) crystalline resins,
- (2) elastomers incompatible with the crystalline resins and having heat resistance higher than that of the crystalline resin,
- (3) materials having compatibility with both of the crystalline resins and the elastomers (compatible materials), and
- (4) electrically conductive particles.

5. A temperature self-controlling heating composition of Claim 4, in which each content of the crystalline resins, elastomers, the compatible materials and the electrically conductive particles is about 15 to about 60 % by weight, about 15 to about 60 % by weight, about 5 to about 30 % by weight, and about 10 to about 60 % by weight in the above order.

6. A temperature self-controlling heating composition of Claim 4 or 5, in which the elastomer possesses an affinity to the electrically conductive particles rather than to the crystalline resin and the compatible materials.

7. A temperature self-controlling heating composition of any one of Claims 1 to 6, in which the crystalline resins are polyethylene or modified polyethylenes.

8. A temperature self-controlling heating composition of any one of Claims 1 to 7, in which the elastomers are thermoplastic elastomers.

9. A temperature self-controlling heating composition of any one of Claims 1 to 8, in which the electrically conductive particles are carbon black.

10. A temperature self-controlling heating composition of any one of Claims 1 to 9, in which the electrically conductive particles are mainly dispersed in the elastomer.

11. A temperature self-controlling heating composition of any one of Claims 3 or 6 to 10, in which the affinity to the electrically conductive particles is given by a maleic anhydride group and the particles are carbon black.

12. A temperature self-controlling heating composition of any one of Claims 4 to 11, in which the compatible materials are resinous materials.

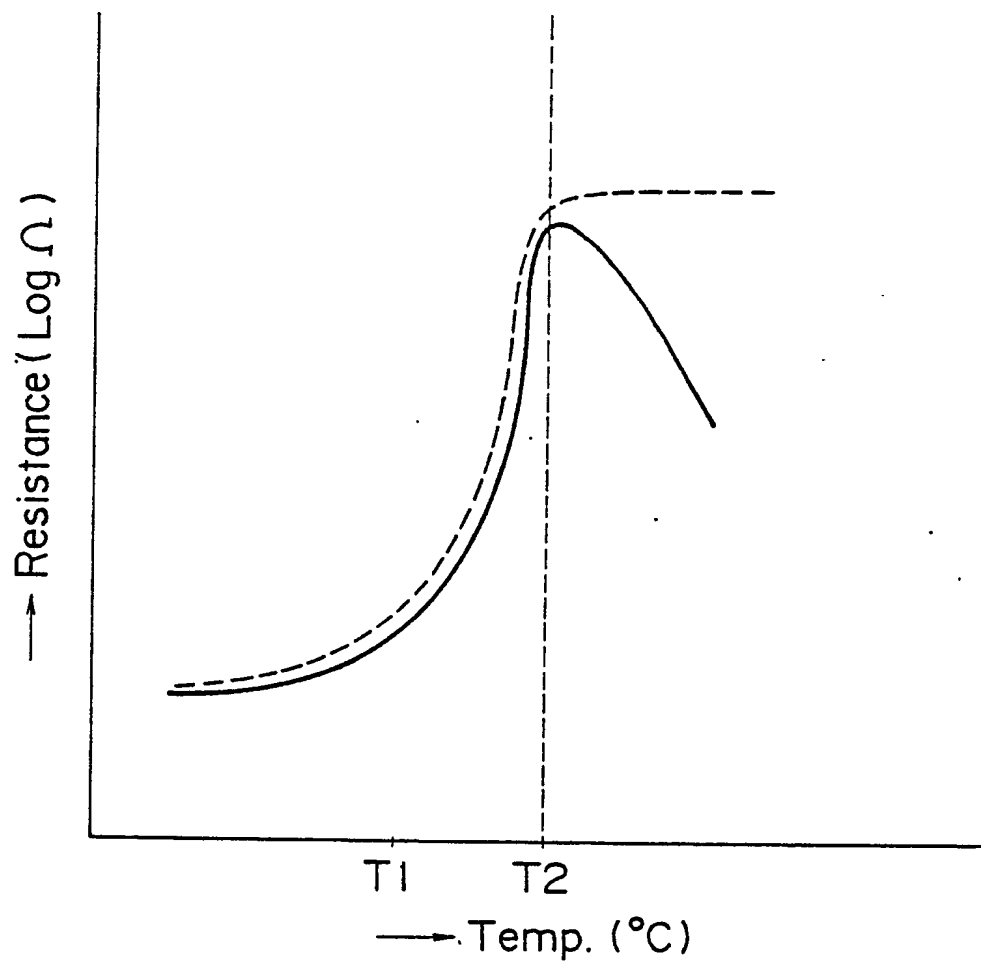
Fig. 1

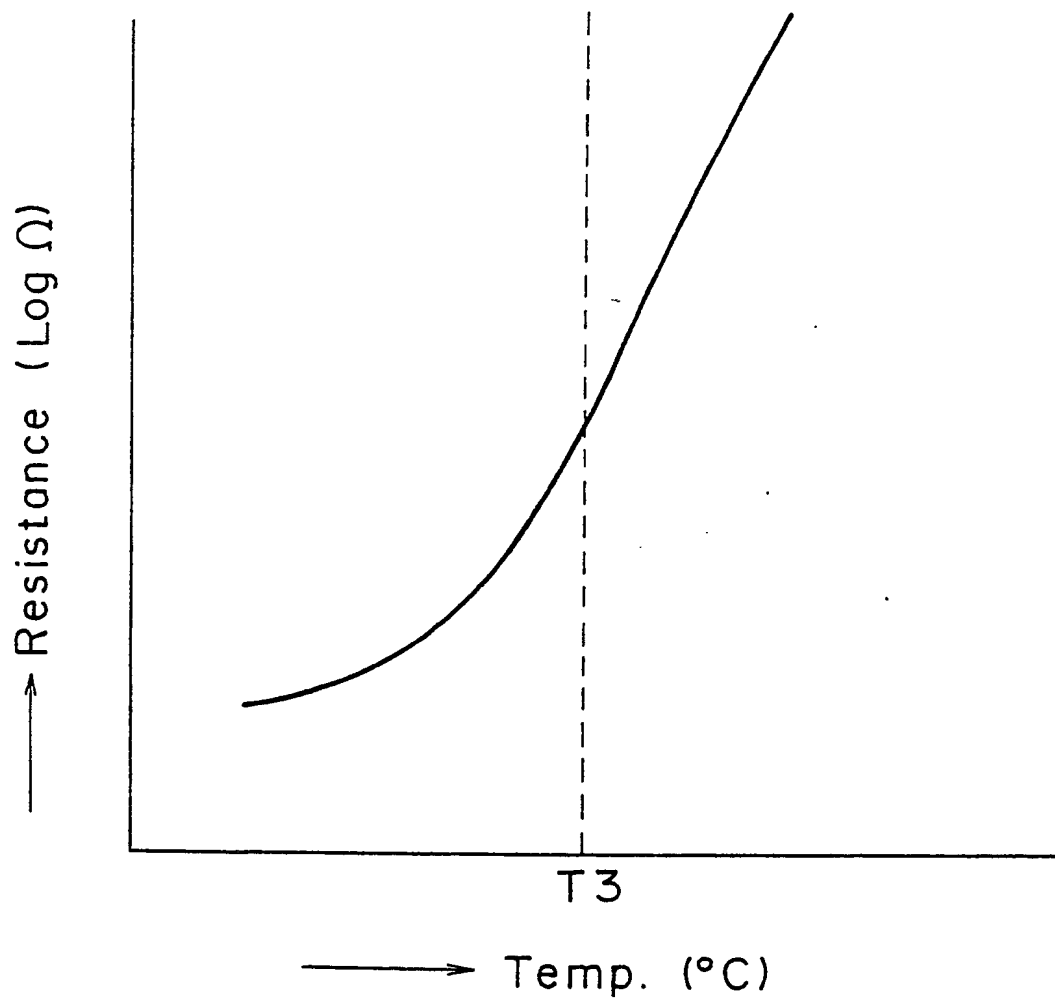
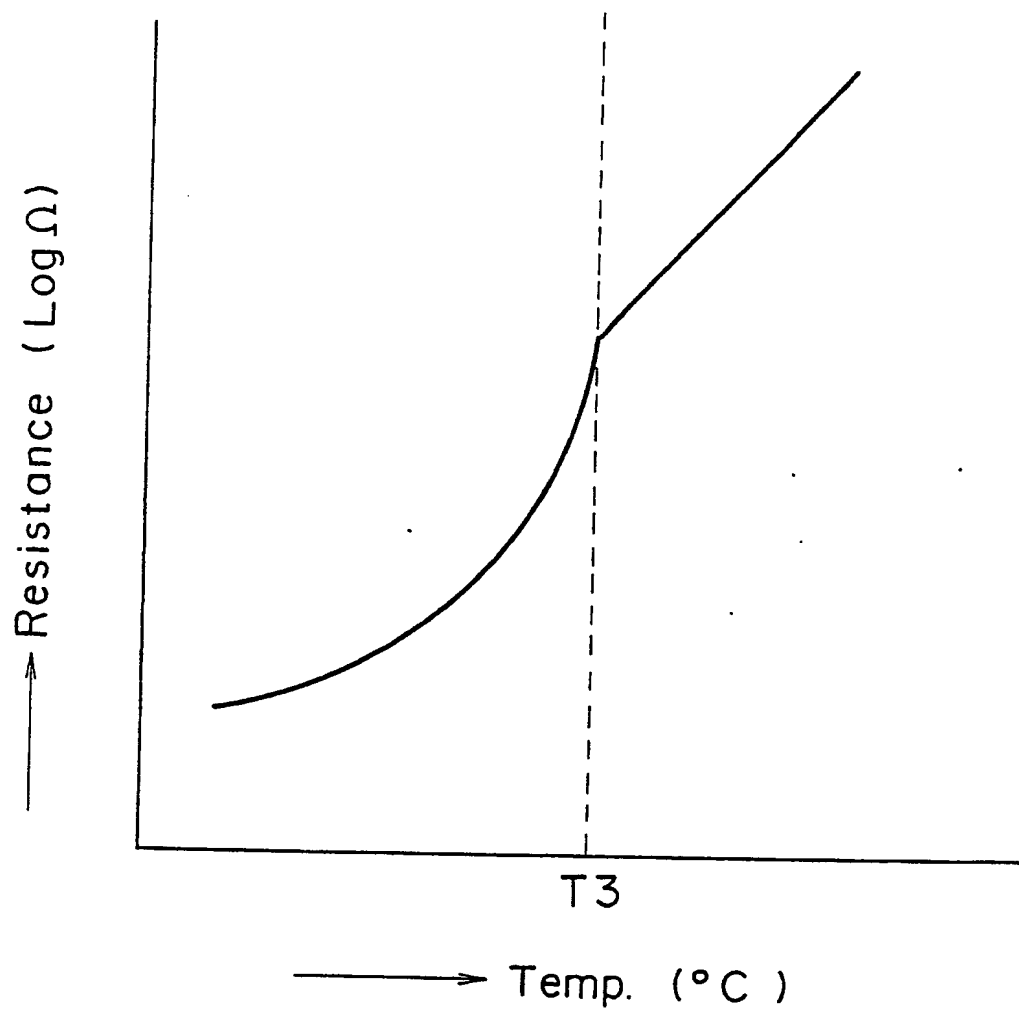
Fig. 2

Fig. 3



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89109788.3
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	<u>US - A - 4 658 121</u> (HORSMA) * Abstract; column 6, line 64 - column 9, line 28; claims 1,4,5,7-16 *	1,2,4, 5,7-9, 11	H 05 B 3/10 H 05 B 1/02
A	<u>EP - A2 - 0 040 537</u> (RAYCHEM) * Abstract; page 4, lines 9-21 *	1,4,7- 9,11	
A	<u>US - A - 4 177 446</u> (DIAZ) * Column 1, line 52 - column 2, line 22; column 5, lines 24-61; claims 1-4 *	1,4,7- 9,11	
A	<u>US - A - 3 823 217</u> (A.J.KAMPE) * Column 1, lines 44-50; column 2, lines 52-72; column 3, lines 21-55; claims 1-7 *	1,4,7, 9,11	
A	<u>EP - A1 - 0 098 253</u> (KIMA) * Page 5, lines 14-20; fig. 2 *	1,4	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 08-09-1989	Examiner TSILIDIS
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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